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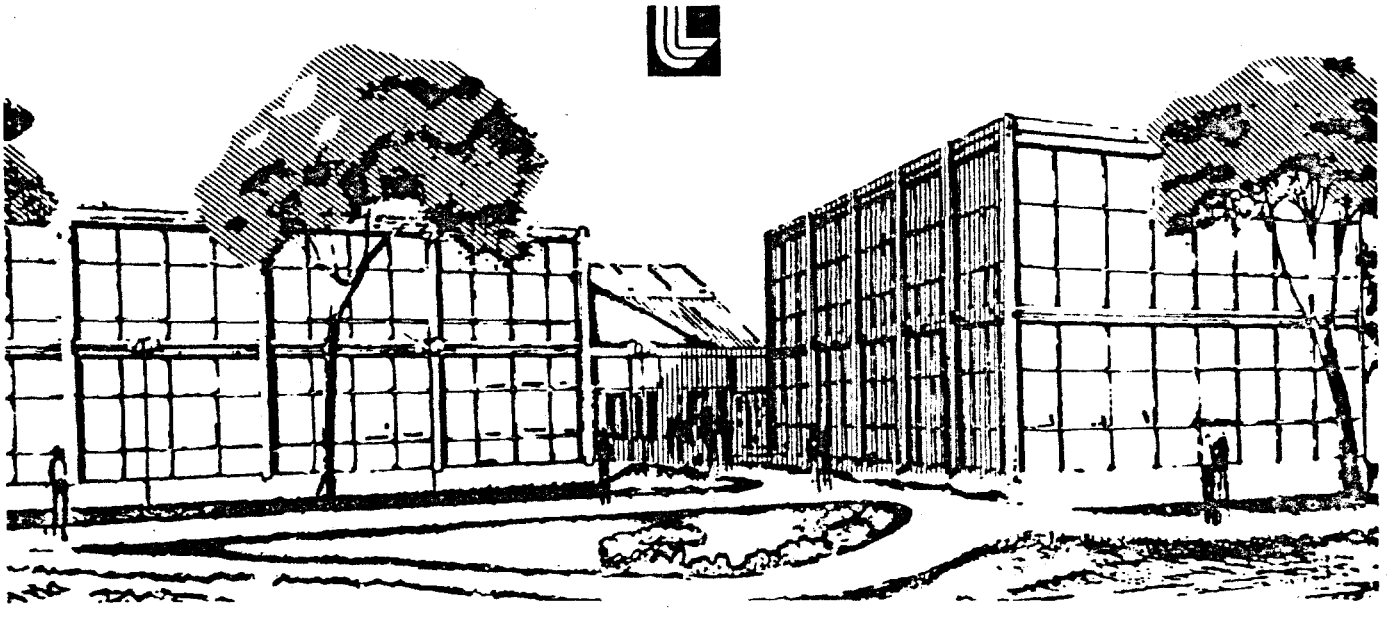

COLLISIONAL EFFECTS IN CARBON-13 ENRICHMENT BY CO_2 LASER[†]

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ABSTRACT

Collisional effects have been evaluated in carbon-13 enrichment by multiple-photon dissociation of CF_3Br at 9.6μ. Dissociation yields of both isotopic species increase with pressure. The single-step C-13 enrichment in C_2F_6 photoproduct falls suddenly above 1 torr. Shortening the dissociation pulse to 2 nanoseconds permits operation to 225 torr.

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SUMMARY

CO_2 laser multiple-photon dissociation of small halocarbon molecules has emerged as a very attractive route to enrichment of carbon-13.[1] Dissociation of CF_3Br near 9.6μ results in a single-step carbon-13 enrichment factor of 50-60, and is perhaps the best molecule for photochemical carbon-13 enrichment at room temperature.[1] We have examined the collisional effects in this process and have observed both an increase in photoproduct yield and a decrease in isotopic enrichment due to collisions. Under conditions of very low energy deposition, at wavelength of low molecular absorption coefficient, an increase in single-step enrichment occurs with increasing pressure, up to a critical pressure. Carbon-13 enrichment occurs via the steps

$$^{13}CF_3Br + nh\nu\ (9.6\mu) \rightarrow {}^{13}CF_3 + Br \qquad (1)$$

$$^{13}CF_3 + {}^{13}CF_3 \rightarrow {}^{13}C_2F_6 \qquad (2)$$

Both photoproduct yields and carbon-13 enrichment were determined from the C_2F_6 product. C_2F_6 product yields were determined by gas chromatography with TC detection, and carbon-13 enrichment determined from the mass 119, 120, 121 peaks of the C_2F_5 fragment in mass spectrometry.

At P(24), 9.6μ, the dissociation probability of $^{13}CF_3Br$ was 10% below 0.1 torr pressure at an energy fluence of 26 J/cm^2. Collisions increased

the $^{13}CF_3Br$ dissociation probability monotonically to 100% as the total CF_3Br (containing 1.1% $^{13}CF_3Br$) was increased to 5 torr using a laser pulse duration of about 100 nanoseconds. However, the $^{12}CF_3Br$ dissociation yield also rose from 0.2% to 100% over the same pressure range. The net effect on the single-step enrichment factor is shown in the left-most curve of Figure 1. Figure 1 indicates a very sudden 40-fold drop in the C-13 enrichment factor as pressure doubles from 1 to 2 torr. We attribute this to a "thermal avalanche" effect. As pressure increases, absorption and hence energy loading within the focal volume of the laser beam increases. This local heating leads to population of higher J states in $^{12}CF_3Br$, which can now be excited by the laser beam leading to still further heating and increased absorption. The chosen wavelength of P(24), 9.6μ is very much in the long-wavelength wing of $^{12}CF_3Br$ absorption, and very little $^{12}CF_3Br$ normally resides in these high J states. To verify this explanation, CF_3Br was dissociated at P(36), 9.7μ, where very little absorption occurs for either isotopic species. Under these conditions of weak absorption the "thermal avalanche" did not occur until 5 torr. In fact, the single-step C-13 enrichment factor increased from 40 at 0.2 torr to 65 at 2 torr. An increase in isotopic enrichment factor with pressure has also been observed in hexafluoroacetone.[2] Above 4 torr the "thermal avalanche" effect resulted in an order-of-magnitude decrease in the C-13 enrichment factor with only 20% increase in CF_3Br pressure.

A dramatic improvement in the operating pressure limits in carbon-13 enrichment was achieved by shortening the CO_2 laser pulse duration to 2 nanoseconds (short-pulse experiments were performed at the Los Alamos Scientific Laboratory in collaboration with Scott J. Thomas). Under these irradiation

conditions at the same P(24) wavelength, no "thermal avalanche" effect was observed. Results are shown in Figure 1, right-hand curve, and indicate only a very slow decrease in carbon-13 enrichment out to 225 torr, the maximum pressure utilized. Additional details of carbon-13 enrichment will be discussed.

(1) M. Drouin et al., Chem. Phys. Lett. 60, 16 (1978).

(2) P. A. Hackett, M. Gauthier, C. Willis, and R. Pilon, J. Chem. Phys. 71, 546 (1979).

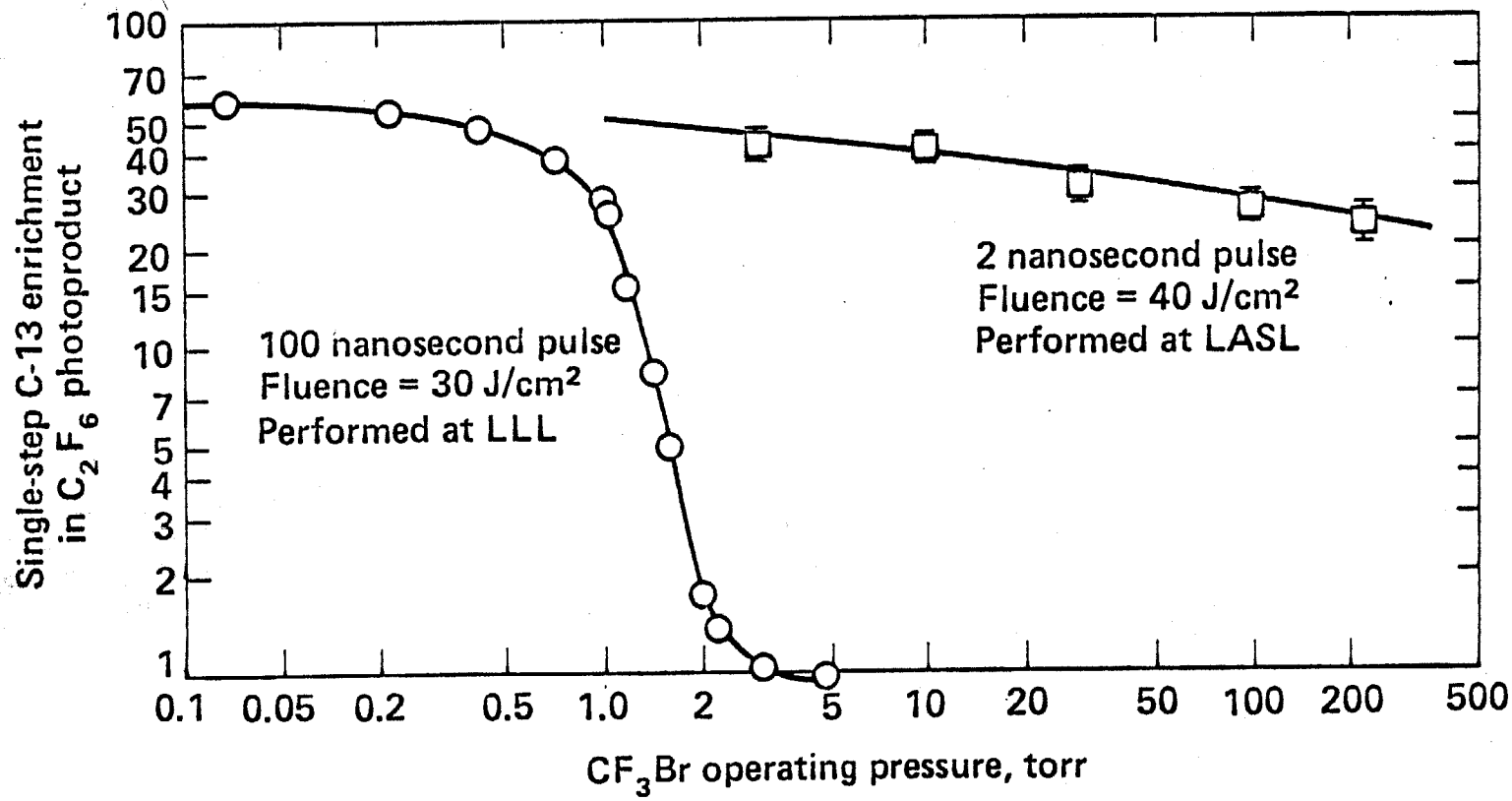

FIGURE 1

CO_2 laser techniques can be applied very effectively in separation of light isotopes such as carbon-13. This figure shows that the single-step carbon-13 enrichment factor is about 50 at low pressure using CF_3Br. The CF_3Br dissociates by high power pulsed CO_2 laser (P(24), 9.6μ) to yield carbon-13 enriched $^{13}CF_3$ fragments that recombine to produce $^{13}C_2F_6$. The $^{13}C_2F_6$ may be then converted into the desired C-13 bearing products, or it may undergo further laser enrichment to yield nearly pure carbon-13. The sharp decrease in C-13 enrichment at higher pressure may be greatly reduced by using shorter duration CO_2 laser pulses, as shown in the curve to the right. Higher pressure operation greatly increases the throughput and greatly reduces the photochemical reactor size.